



Non isothermal model free kinetics for pyrolysis of rice straw



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HIGHLIGHTS

- Study of pyrolysis behavior and kinetics of rice straw.
- Indication of complex multistep mechanism for RS pyrolysis using isoconversional plot.
- Determination of reaction mechanism using master plots and compensation effects.
- Isothermal predictions from non-isothermal data for validation of kinetic results.

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ABSTRACT

The kinetics of thermal decomposition of rice straw was studied by thermogravimetry.

Non-isothermal thermogravimetric data of rice straw decomposition in nitrogen atmosphere at six different heating rates of 5–40 °C/min was used for evaluating kinetics using several model free kinetic methods. The results showed that the decomposition process exhibited two zones of constant apparent activation energies. The values ranged from 142 to 170 kJ/mol ($E_{\text{avg}} = 155.787$ kJ/mol), and 170 to 270 kJ/mol ($E_{\text{avg}} = 236.743$ kJ/mol) in the conversion range of 5–60% and 61–90% respectively. These values were used to determine the reaction mechanism of process using master plots and compensation parameters. The results show that the reaction mechanism of whole process can be kinetically characterized by two successive reactions, a diffusion reaction followed by a third order rate equation. The kinetic results were validated using isothermal predictions. The results derived are useful for development and optimization of biomass thermochemical conversion systems.

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1. Introduction

Environmental protection and fossil fuel depletion are some of the driving forces which push technological research towards the development of alternative fuels. Second generation biofuels from biomass is an interesting route, able to transform an abundant and well distributed feedstock into fuels with properties similar to conventional fossil fuels (Mendes and Figueiredo, 2011). Biomass is a source of short-cycle carbon, which is of utmost importance for future energy needs (Wongsiriamnuay and Tippayawong, 2010). Moreover the lignocellulosic biomass is low in sulfur, resulting in a more ecological fuel (Catoire et al., 2008). Thermochemical conversion is one of the main approaches used to produce bio-oils, derived from the de-polymerization and fragmentation reactions of the three key biomass building blocks: cellulose, hemicellulose and lignin (Guillaume and Thierry, 2013). The variation in thermal response exhibited by biomass is

attributed to the varying proportion of these constituents from biomass to biomass. Biomass can be converted into useful forms of energy using thermo-chemical and bio-chemical processes but thermo-chemical conversion technology finds its dominance because of its high efficiency in conversion to gaseous, liquid and solid products under thermal conditions (Zhang et al., 2006).

Pyrolysis can be used as an independent process for the production of useful energy holders (fuels) and/or chemicals. It also occurs as the first step in a gasification or combustion process. The development of thermochemical processes for biomass conversion and proper equipment design requires the knowledge of several process features which include a good understanding of the governing pyrolysis mechanisms, the determination of the most significant pyrolysis parameters and of their effect on the process and knowledge of the kinetics (Koufopoulos et al., 1989). A precise conception of solid state pyrolysis kinetics is very crucial in designing and operating industrial biomass conversion systems. Thermogravimetric analysis (TGA) is the most commonly applied thermoanalytical technique in solid-phase thermal decomposition studies (Ninan, 1989), and it has gained extensive recognition in thermal studies of biomass pyrolysis.

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The precision and accuracy of the kinetic expression governing the reaction mechanism and the kinetic parameters inferred from kinetic analysis have a profound dependence on the reliability of the evaluation methods used to study the decomposition behavior of biomass under different conditions of temperature and/or atmosphere. Numerous researchers have investigated the decomposition kinetics of biomass using model fitting approaches involving global or semi-global mechanisms. Di Blasi presented a comprehensive review of the different classes of mechanisms proposed for the pyrolysis of wood and other cellulosic materials (Di Blasi, 1993). One step global model involving a single global reaction has been used widely but it is extremely simplified and is unsuitable to predict the complex nature of decomposition of biomass (Varhegyi et al., 1989). Varhegyi used the independent reaction model of three pseudo-components. This model ensures the possibility of simultaneous decomposition of pseudo components. The biomass decomposition results reported in the literature (Varhegyi et al., 1997; Orfao et al., 1999; Gronli et al., 2002) show that this model provides consistent parameter values with low fitting errors. The macroscopic kinetics of biomass pyrolysis is complex as it includes information about simultaneously occurring multiple steps. Unraveling the macroscopic kinetics presents a certain challenge that can only be met by the computational methods that allow for detecting and treating multi-step processes (Vyazovkin and Sbirrazzuoli, 2006). According to the results of the ICTAC Kinetics Project (Brown et al., 2000), isoconversional methods are among a few methods that are up to this challenge.

This study aims to investigate the characteristics and kinetics that describes the thermal decomposition process of rice straw. Rice straw is one of the main cereal straws and is created as by-product of the rice milling processes in large quantities worldwide every year. Asia contributes to total production of rice straw with an important ratio of 92% (Putun and Apaydin, 2004). The pyrolysis behavior of rice straw is investigated using thermogravimetric analyzer. Isoconversional analysis methods, generalized master plots are used to determine the kinetic triplet. The work compares the different isoconversional methods available for kinetic analysis in detail for rice straw and provides basis for further applications of the thermochemical conversion of rice straw as a potential feedstock.

2. Experimental method

2.1. Sample preparation and characterization

The rice straw sample used in the study was subjected to several treatments before analysis. It was dried at room temperature and was milled and sieved to an average particle size of 50 μm . The Moisture content of the feed has been obtained from the HR-83 Mettler Toledo Halogen Moisture Analyzer. The calorific value measured using a Parr 6300 bomb calorimeter came out to be 13.414 MJ/kg. The proximate analysis of rice straw sample showed that it contains 11.95% moisture, 19.74% ash and fixed carbon of 7.25%. The volatile content of rice straw was 73.015%. The ultimate analysis showed that rice straw contains 34.11% carbon, 6.52% hydrogen, 0.174% nitrogen and sulfur less than 0.1 wt%. The oxygen content was calculated by difference and was found as 59.2%. The trace metal analysis of rice straw sample has been carried out in the DRE, PS-3000 UV, Leeman Labs Inc., Inductively Coupled Plasma- Atomic Emission Spectroscopy. A high content of silica of 1,04,235 ppm is found in rice straw. The elemental analysis showed presence of potassium (17,360 ppm), calcium (8161 ppm), magnesium (1077 ppm), aluminum and manganese with traces of sodium, zinc, copper, and lead in rice straw.

2.2. Experimental techniques

The experiments were carried out in a thermogravimetric analyzer, DTG-60 (Shimadzu, Japan), to measure and record the sample mass change with temperature over the course of the pyrolysis reaction. Rice straw samples of average particle size of 50 μm were taken in alumina crucibles with sample mass in the range of ca. 10 mg. The samples were heated from room temperature to 700 $^{\circ}\text{C}$ at six different heating rates of 5, 10, 20, 30 and 40 $^{\circ}\text{C}/\text{min}$ and the results obtained were used in the kinetic analysis. Nitrogen gas at a flow rate of 100 ml/min was used as an inert purge gas to displace air in the pyrolysis zone, thus avoiding unwanted secondary reactions and oxidation of the sample. The experimental results were tested to ensure reproducibility.

2.3. Kinetic models-theoretical background

The fundamental equation used for study of kinetics of heterogeneous solid-state thermal decomposition can be described as follows,

$$\frac{d\alpha}{dt} = kf(\alpha) = A \exp\left(\frac{-E_x}{RT}\right)f(\alpha) \quad (1)$$

where, the reaction rate ($d\alpha/dt$) can be expressed as a function of a temperature dependent term $k(T)$ and the dependence of extent of conversion (α) on reaction model $f(\alpha)$. The value of α typically reflects the progress of the overall transformation of a reactant to products. The overall transformation can generally involve more than a single reaction or, in other words, multiple steps each of which has its specific extent of conversion (Vyazovkin et al., 2011).

The rate constant $k(T)$ is generally expressed by Arrhenius equation as follows,

$$k(T) = A \exp\left(\frac{-E_x}{RT}\right) \quad (2)$$

where A is the pre exponential factor (in min^{-1}), E_x is the apparent activation energy (in kJ/mol), T is the temperature (in K) and R is the gas constant (8.314 kJ/mol K). The conversion α can be defined as

$$\alpha = \frac{m_0 - m_t}{m_0 - m_{\infty}} \quad (3)$$

where m_0 is the initial sample weight, m_t is the sample weight at time, t , and m_{∞} is the final sample weight. For dynamic analysis of non-isothermal data a term β as the heating rate (in K/min) is introduced into the equation and the final equation obtained is as follows,

$$\frac{d\alpha}{dT} = k(T)f(\alpha) = \frac{A}{\beta} \exp\left(\frac{-E_x}{RT}\right)f(\alpha) \quad (4)$$

The various methods for kinetic analysis can be broadly classified into two groups as “model fitting kinetics” and “model free kinetics”. Model fitting methods involve forcible fitting of kinetic parameters into the equation which results in ambiguous kinetic interpretations where more than one reaction mechanism satisfactorily fits into the data at the cost of drastic variations in the Arrhenius parameters, which compensate for the difference between the assumed form of $f(\alpha)$ and the true but unknown reaction model (Vyazovkin and Wight, 1999). The model-free approach does not require assumption of specific reaction models, and yields unique kinetic parameters as a function of either conversion (isoconversional analysis) or temperature (non parametric kinetics) (Vyazovkin, 2000). Of the two main model free methods the isoconversional approach is more frequently adopted, and is increasingly being used in biomass thermochemical conversion research (Aboyade et al., 2012).

2.3.1. Isoconversional analysis methods

Isoconversional techniques are based on the isoconversional principle which states that at a constant extent of conversion, the reaction rate is a function only of the temperature so that (Vyazovkin and Sbirrazzuoli, 2006).

$$\left[\frac{d \ln \left(\frac{d\alpha}{dT} \right)}{dT^{-1}} \right]_{\alpha} = -\frac{E_{\alpha}}{R} \quad (5)$$

Isoconversional kinetics rest upon evaluating a dependence of the effective activation energy on conversion based on thermogravimetric data from multiple heating rates and using this dependence for making kinetic predictions and for exploring the mechanisms of thermal processes (Vyazovkin, 2008). Isoconversional methods can be divided in two separate classes based on the basic equation they use for defining their model equation as differential and integral analysis methods. Differential methods use the fundamental solid state equation (Eq. (1)) whereas the integral methods are based on the integral form of the non-isothermal rate law given as follows,

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \int_0^T \frac{A}{\beta} \exp \left(\frac{-E}{RT} \right) dT \quad (6)$$

The different isoconversional methods used for kinetic analysis of rice straw are as follows,

2.3.1.1. Friedman method. The Friedman method (Friedman, 1964) is the most straight forward and the most common differential isoconversional method to evaluate the effective activation energy, E_a , as a function of the extent of reaction. Friedman gave the following equation

$$\ln \left(\frac{d\alpha}{dT} \right) = \ln \left[\beta_i \left(\frac{d\alpha}{dT} \right)_{\alpha,i} \right] = \ln [A_{\alpha} f(\alpha)] - \frac{E_{\alpha}}{RT_{\alpha,i}} \quad (7)$$

where the subscript α refers to the value related to a considered conversion, and i to a given heating rate. If the mechanism of the process does not depend on the heating rate, the $f(\alpha)$ value at constant value of α also does not depend on it. In the plot of $\ln [\beta_i (\frac{d\alpha}{dT})_{\alpha,i}]$ against $1/T_i$, the value of slope gives value of activation energy as a function of conversion (independent of the $f(\alpha)$ -model). The Friedman method can be applied to any thermal history and any temperature program.

2.3.1.2. Kissinger Akahira and Sunose method. Kissinger–Akahira–Sunose method (Kissinger, 1957; Akahira and Sunose, 1971) is an isoconversional linear integral method based on the following equation:

$$\ln \frac{\beta}{T^2} = \ln \frac{AR}{E_a g(\alpha)} - \frac{E_a}{RT} \quad (8)$$

For a constant value of conversion (α), the plot $\ln(\beta/T^2)$ vs. $1/T$, obtained from thermograms recorded at several heating rates, yield a straight line whose slope allows evaluation of the apparent activation energy. This method is referred as KAS in the paper.

2.3.1.3. Flynn Wall Ozawa method. Ozawa Flynn Wall method (Ozawa, 1965; Flynn and Wall, 1966) uses Doyle's equation for approximation of temperature integral. This is an isoconversional linear integral method based on the equation:

$$\ln \beta = \ln \frac{AE}{Rg(\alpha)} - 5.331 - 1.052 \frac{E}{RT} \quad (9)$$

Plots of $\ln \beta$ vs. $1/T$, at fixed value of conversion help in evaluating the activation energy from the slope of straight line plot. This method is referred as FWO in the paper.

2.3.1.4. Vyazovkin method. Vyazovkin equation is an exact non-linear equation used to increase the accuracy of evaluating the activation energy by the isoconversional method. The Vyazovkin method is based on the following equation for determination of activation energy value (E_{α}) at any particular value of α which minimizes the following function,

$$\phi = \sum_i^n \sum_{j \neq i}^n \frac{I(E_{\alpha}, T_{\alpha,i}) \beta_j}{I(E_{\alpha}, T_{\alpha,j}) \beta_i} = \min \quad (10)$$

In this equation,

$$I(E_{\alpha}, T_{\alpha}) = \int_0^{T_{\alpha}} \exp \left(\frac{-E}{RT} \right) dT \quad (11)$$

Substituting experimental values of T and β into this equation and varying E_{α} to reach the minimum value of this function gives the value of the activation energy at a given conversion. The values of $I(E_{\alpha}, T_{\alpha,i})$ are calculated with the help of an accurate Senum–Yang approximation (Vyazovkin, 1997). The minimization procedure is repeated for each value of α to find the dependence of the activation energy on the extent of conversion.

2.3.1.5. Vyazovkin AIC (advanced isoconversional) method. Vyazovkin gave a modified integral isoconversional method, in which the constancy of E_{α} is assumed for only a small segment $\Delta\alpha$ and the integral with the limits $T_{\alpha-\Delta\alpha}$ and T_{α} ($t_{\alpha-\Delta\alpha}$ and t_{α}) is evaluated numerically from the non-isothermal data by using trapezoidal rule. This method avoids the undesirable flattening of E_{α} versus α curve which is a drawback of the regular vyazovkin method due to averaging of E_{α} values in the range from 0 to α (Vyazovkin, 2001). The following equations describe the Vyazovkin AIC method.

$$J(E_{\alpha}, T(t)) = \int_{T_{\alpha-\Delta\alpha}}^{T_{\alpha}} \exp \left(\frac{-E}{RT(t)} \right) dt \quad (12)$$

$$\phi = \sum_i^n \sum_{j \neq i}^n \frac{I(E_{\alpha}, T_i(t_{\alpha}))}{I(E_{\alpha}, T_j(t_{\alpha}))} = \min \quad (13)$$

where $T_i(t)$ ($i = 1 \dots n$) are actual variations of the temperature. Substituting the time, t_{α} , for which a given conversion has been reached and the actual temperature T_i at that moment, into above equation and varying E_{α} until the minimum is attained gives an estimate of the activation energy (Vyazovkin, 1997). The temperature integral is calculated using trapezoidal rule for numerical integration.

2.3.1.6. Iterative linear integral isoconversional method. Cai and Chen (2009) proposed the iterative linear integral isoconversional method. For a series of nonisothermal curves, $i = 1, 2, 3 \dots n$, the equation for iterative linear method is as follows:

$$\ln \left\{ \frac{\beta_i}{T_{\alpha,i}^2 \left[h(x_{\Delta\alpha,i}) - \frac{x_{\alpha,i}^2 e^{x_{\alpha,i}}}{x_{\alpha-\Delta\alpha,i}^2 e^{x_{\alpha-\Delta\alpha,i}}} h(x_{\alpha-\Delta\alpha,i}) \right]} \right\} = \ln \left[\frac{\frac{A_{\alpha-\Delta\alpha/2}}{R}}{E_{\alpha-\Delta\alpha/2} g(\alpha, \alpha - \Delta\alpha)} \right] - \frac{E_{\alpha-\Delta\alpha/2}}{RT_{\alpha,i}} \quad (14)$$

where, $x_{\alpha} = \frac{E_{\alpha-\Delta\alpha/2}}{RT_{\alpha}}$ and $x_{\alpha-\Delta\alpha} = \frac{E_{\alpha-\Delta\alpha/2}}{RT_{\alpha-\Delta\alpha}}$

The temperature integral was approximated by a function $h(x)$ as follows:

$$I(E, T) = \int_0^T e^{-\frac{E}{RT}} dT = \frac{RT^2}{E} e^{-\frac{E}{RT}} h(x) \text{ where } h(x) = x^2 e^x \int_x^{\infty} \frac{e^{-x}}{x^2} dx$$

The $h(x)$ function has no analytical solution and can be solved numerically.

The above equation is a linear equation, provided that $g(\alpha, \alpha - \Delta\alpha)$ is constant at fixed conversion (α). The linear plot of this relationship obtained allows evaluation of $E_{\alpha-\alpha/2}$.

However, $\ln \left\{ \beta_i / T_{\alpha,i}^2 \left[h(x_{\alpha,i}) - \frac{x_{\alpha,i}^2 e^{x_{\alpha,i}}}{x_{\alpha-2,i}^2 e^{x_{\alpha-2,i}}} h(x_{\alpha-2,i}) \right] \right\}$ is a function of $E_{\alpha-\alpha/2}$. Therefore, an iterative procedure is used. The details of the steps can be found in the paper of Cai and Chen (2009). The iterative linear integral isoconversional method for the determination of the dependence of the activation on the conversion degree is based on the integration over low ranges of the conversion degree and temperature.

2.3.2. Evaluation of pre-exponential factor and reaction mechanism $f(\alpha)$ for model free methods

Isoconversional methods are controversial in evaluation of pre exponential factor and reaction mechanism and the constraints involved do not permit a straight forward evaluation of the remaining kinetic parameters A and $f(\alpha)$. Several methods have been proposed for evaluation of these parameters. The methods used in the present study are selected as such to clarify the status and potential of isoconversional methods to evaluate the remaining kinetic parameters. A brief description of the methods used in this investigation is as follows:

2.3.2.1. Using compensation parameters. An apparent compensation effect is observed when a model fitting method is applied to a single-heating rate run. Substitution of different models $f(\alpha)$ into a rate equation (Eq. (4)) and fitting it to experimental data yields different pairs of the Arrhenius parameters, A_i and E_i (Lesnikovich and Levchik, 1983). The models $f(\alpha)$ used in evaluation are given in Table 1.

Although the parameters vary widely with the selected model $f(\alpha)$, they all demonstrate a strong correlation known as a compensation effect:

$$\ln A_i = \alpha^* + \beta^* E_i \quad (15)$$

where α^* and β^* are constants (the compensation effect parameters). For each heating rate, β_v , using an integral or differential method, the pairs (A_{vj}, E_{vj}) , characteristic for each conversion function $f(\alpha)$, are determined using any form of equation (differential or integral). Using the relation of the apparent compensation effect, for each heating rate the compensation parameters (α_v^*, β_v^*) are determined. Now using these compensation parameters (α_v^*, β_v^*) the A_x is obtained at using E_x values at each conversion value.

$$\ln A_x = \alpha^* + \beta^* E_x \quad (16)$$

The parameters E and $\ln A$ obtained by the model-fitting procedure are only used here to evaluate the relationship that exists between E and $\ln A$. The objective of the method proposed is not to give an interpretation of the compensation effect and its origins remain the subject of debate. If a compensation effect is observed, then the above method can be used to compute a model-free value of $\ln A_x$ for each value of E_x obtained by means of an isoconversion method (Sbirrazzuoli, 2013). When A_x and E_x values are obtained at each conversion value $f(\alpha)$ can be obtained numerically by putting the values of A_x and E_x in Eq. (1).

2.3.2.2. $z(\alpha)$ master plots. The $z(\alpha)$ plots are derived by combining the integral and differential forms of reaction model.

$$z(\alpha) = f(\alpha) * g(\alpha) \quad (17)$$

$$z(a) = \frac{d\alpha}{dt} \exp\left(\frac{E_x}{RT_x}\right) \int_0^{T_x} \exp\left(\frac{-E_x}{RT}\right) \quad (18)$$

The temperature integral is approximated by fourth rational expression of Senum-Yang approximation which gives lower errors for conversion values of $\alpha > 0.2$. The temperature integral solved using trapezoidal rule yields less errors in comparison with Senum-Yang approximation, which proves that Senum Yang approximation yields good values at lesser computation. The theoretical and experimental $z(\alpha)$ curves are compared and the best fit model is determined. Once the reaction model is identified the pre-exponential factor is also determined from any of the integral or differential rate expression.

3. Results and discussion

3.1. Thermogravimetric analysis (TGA)

The TG and DTG curves of rice straw in inert atmosphere of nitrogen at different heating rates are shown in Figs. 1a and 1b respectively.

In general, the pyrolysis process can be divided into three stages: moisture evaporation, main devolatilization (active pyrolysis zone) and continuous slight devolatilization (passive pyrolysis zone). The deconvolution of DTG curve shows presence of these three stages in rice straw and three peaks can be seen in respective temperature ranges. The first zone till 150 °C can be attributed to the removal of moisture and absorbed water. A minor weight loss of 7.36 wt% is seen in this zone. The second region corresponds to active pyrolysis zone and corresponds to the temperature range of 150 °C to 350 °C. This is the major zone for pyrolysis process as maximum devolatilization takes place in this zone. Two major peaks are visible in the deconvoluted curve in this zone and can be related to hemicellulose and cellulose decomposition with peak maxima at temperatures of 285.9 °C and 313.8 °C respectively. The peaks of hemicellulose and cellulose are merged in this region to give a broader peak for the second region. The third zone can be related to the passive pyrolysis zone (350–700 °C) where lignin decomposition is prominent and reflects a weight loss of 10.8%. Lignin decomposition starts at 210 °C and lasts to 600 °C; hence lignin is decomposed in both regions of active and passive pyrolysis. Lignin decomposes slowly over a wide temperature range and is responsible for the long tailing of DTG curve. The total weight loss till 900 °C is 43.48%. The weight loss reported in literature is about 59% for rice straw (Ji et al., 2011).

TG and DTG curves of rice straw were recorded at six different heating rates of 5, 10, 15, 20, 30, 40 °C/min respectively. The effect of heating rate on TG and DTG curves can be seen in Figs. 1a and 1b. Heating rate affects the TG curve positions, maximum decomposition rate and location of peak maxima T_m . The main decomposition zone observed in DTG curve shifts to higher temperature range with an increase of heating rate. When heating rate increases, starting and final temperature of active and passive pyrolysis region also increase. The moisture decomposition region does not exhibit a greater variation with change of heating rate.

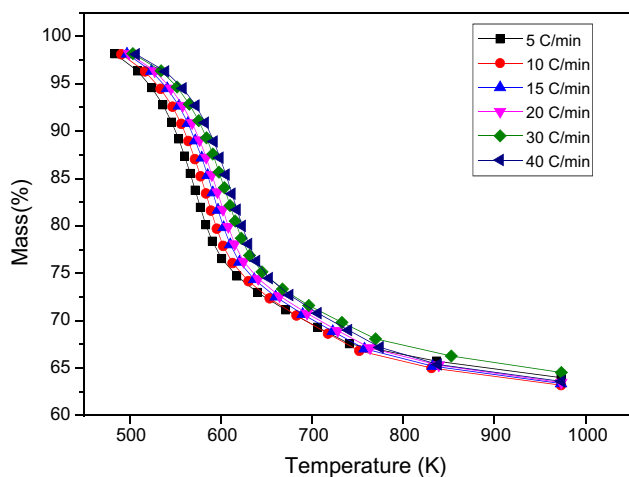
3.2. Kinetic analysis results

In this study, the results obtained from thermogravimetric analysis of rice straw at six different heating rates (5, 10, 15, 20, 30 and 40 °C/min) were used with model-free methods to calculate the kinetic parameters. All the isoconversional methods mentioned above i.e. Friedman, KAS, FWO, Vyazovkin, Vyazovkin AIC and Iterative integral method in the conversion range of 2–92% with an increment of 1% under each heating rate were used for kinetic analysis to obtain the isoconversion plot of activation energy E_x with conversion α . The step size of 0.01 is selected as per the recommendations of ICTAC Kinetics Committee, (Vyazovkin et al.,

Table 1

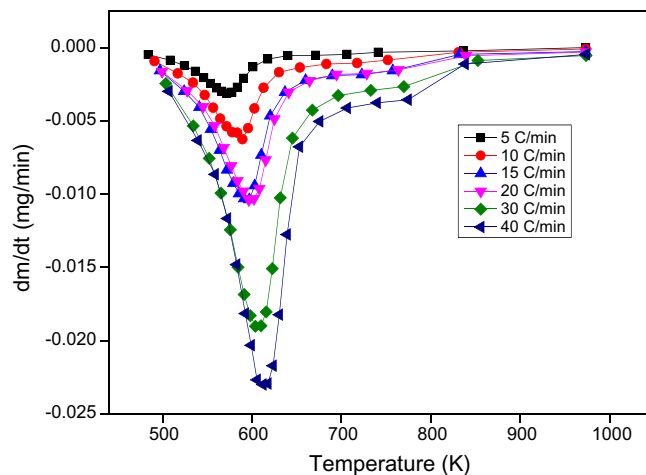
Expressions for $f(\alpha)$ and $g(\alpha)$ functions for some of the common mechanisms operating in solid state reactions.

S. No.	Model	Differential form $f(\alpha)$	Integral form $g(\alpha)$
Nucleation models			
P2	Power law	$(2/3)\alpha^{-1/2}$	$\alpha^{3/2}$
P3	Power law	$2\alpha^{1/2}$	$\alpha^{1/2}$
P4	Power law	$3\alpha^{2/3}$	$\alpha^{1/3}$
P5	Power law	$4\alpha^{3/4}$	$\alpha^{1/4}$
Sigmoidal rate equations			
A1	Avrami-Erofeev	$(3/2)(1-\alpha)[-\ln(1-\alpha)]^{1/3}$	$[-\ln(1-\alpha)]^{2/3}$
A2	Avrami-Erofeev	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
A3	Avrami-Erofeev	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$
A4	Avrami-Erofeev	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	$[-\ln(1-\alpha)]^{1/4}$
F1	Prout-Tompkins	$\alpha(1-\alpha)$	$\ln[\alpha/(1-\alpha)]$
F2	Contracting area	$2(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$
F3	Contracting volume	$3(1-\alpha)^{2/3}$	$-(1-\alpha)^{1/3}$
F4	Random nucleation (1)	$(1-\alpha)^2$	$1/(1-\alpha)$
F5	Random nucleation (2)	$(1-\alpha)^3/2$	$1/(1-\alpha)^2$
Diffusion models			
D1	1D diffusion	$1/2\alpha$	α^2
D2	2D diffusion-Valensi	$[-\ln(1-\alpha)]^{-1}$	$(1-\alpha)$
D3	3D diff-Jander	$(3/2)(1-\alpha)^{2/3}/[1-(1-\alpha)^{1/3}]$	$\ln(1-\alpha) + \alpha$
D4	3D diffusion-Ginstling	$(3/2)/[(1-\alpha)^{-1/3} - 1]$	$[1-(1-\alpha)^{1/3}]^2$
Reaction order models			
R1	First order	$1-\alpha$	$-\ln(1-\alpha)$
R2	Second order	$(1-\alpha)^2$	$(1-\alpha)^{-1} - 1$
R3	Third order	$(1-\alpha)^3$	$[(1-\alpha)^{-2} - 1]/2$

**Fig. 1a.** TG curves of rice straw at different heating rates.

2011) to detect and treat the multistep kinetics. The temperature range for kinetic studies is taken as 150–700 °C as at temperatures less than 150 °C only moisture and physically absorbed water is removed and there is almost negligible weight loss after 700 °C. The apparent activation energy values for all evaluated methods are shown in Table 2. The plots for Friedman method, KAS method and FWO method are shown in Figs. S1, S2, S3 (refer supplementary information).

The correlation coefficients (R) are greater than 0.99 for all curves and all models give a good fit to the experimental data. Values of apparent activation energy are evaluated as a function of conversion by each method. Fig. 2 gives the isoconversion plots

**Fig. 1b.** DTG curves of rice straw at different heating rates.

of apparent activation energy versus conversion for the selected methods.

As it can be seen from the figure, the curves exhibit similar shape corresponding to the considered isoconversional method and the activation energy values are nearly the same. The activation energy values obtained by Friedman method are greater than the values estimated by KAS, FWO and Vyazovkin methods. The curves for KAS, FWO and Vyazovkin are almost overlapping with similar trend. Vyazovkin AIC method gives values greater than the KAS, FWO, Vyazovkin method but less than the Friedman method. The activation energy values obtained by isoconversional methods are termed as 'effective' or 'apparent' activation energy. For a multi step process the activation energy tends to vary throughout the process and hence the term 'effective' activation energy is used. The Friedman method represents an efficient method for evaluation of activation energy as it involves no oversimplified approximation. One major drawback of Friedman method is that it is a differential method, which can be applied to integral data (e.g. TG data) only after numerical differentiation of experimental α vs. T curves that tends to yield quite noisy rate data and, therefore, scattered E_a values. The KAS uses the simple approximation for exponential integral i.e. $p(x) = \exp(-x)/x^2$ and FWO method uses the linear Doyle's approximation to evaluate the temperature integral. Hence, the naive and erroneous approximations involved in these methods results in imprecise and inaccurate values of apparent activation energy. Vyazovkin's method employs the very accurate fourth rationale Senum-Yang approximation for temperature integral which gives errors less than $10^{-5}\%$ and hence can be used efficiently. Vyazovkin's method leads to activation energy values very close to KAS and FWO method due to the undesirable flattening of E_a versus α curve caused by averaging of values in evaluation of integral from 0 to α . Vyazovkin AIC method modifies and increases the accuracy of Vyazovkin method by taking the constancy of activation energy for a small segment $\Delta\alpha$. Trapezoidal rule is used in this paper for evaluation of temperature integral in Vyazovkin AIC method. Hence, Vyazovkin AIC method gives more accurate activation energy values but requires high computation. The iterative linear method was evaluated up to four iterations until which it converged to final values of activation energies. Iterative method gave fluctuating values in comparison with the other methods. For the kinetic studies of rice straw pyrolysis system the nonlinear Vyazovkin AIC method seems to be the best compromise between the stability of calculations and obtaining valid values of actual activation energies in the above-considered range of α .

Table 2
Estimated apparent activation energy value by all kinetic methods.

α	Friedman	KAS	FWO	VYAZOVKIN	V.AIC	Iterative
0.05	168.0815	174.2767	173.4842	174.4459	163.1152	150.4525
0.1	152.9402	144.1295	145.2787	144.3581	143.7449	158.0242
0.15	146.5934	139.7641	141.4021	140.6395	144.2934	129.425
0.2	148.3723	140.7468	142.5441	141.4295	145.4218	139.9953
0.25	149.6824	142.3121	144.1886	142.9323	143.6555	129.0918
0.3	148.6959	139.0388	141.2112	139.6305	146.9409	149.8721
0.35	152.5191	143.0035	145.0836	143.5321	142.5931	144.3747
0.4	155.1646	143.5049	145.6604	144.0424	145.5089	171.3045
0.45	154.8681	143.5647	145.8122	144.1144	149.3317	148.4836
0.5	156.3055	145.7636	147.992	146.2844	148.1446	164.9653
0.55	166.999	150.0801	152.1873	150.6542	147.9113	165.629
0.6	179.5406	154.3104	156.3187	155.0411	159.1277	177.3532
0.65	202.9581	168.3664	169.83	169.3248	176.1884	185.8495
0.7	222.7397	193.2223	193.6941	194.6365	203.5361	200.0583
0.75	244.0404	209.2965	209.3285	209.5722	208.939	238.5702
0.8	246.8805	231.2424	230.6794	231.551	208.0718	234.8829
0.85	281.7985	263.7075	262.083	266.1002	238.9784	250.122
0.9	345.8704	282.4641	280.4652	282.7082	259.7212	313.7305
0.95	281.3286	281.3649	280.756	290.5528	266.641	295.6916

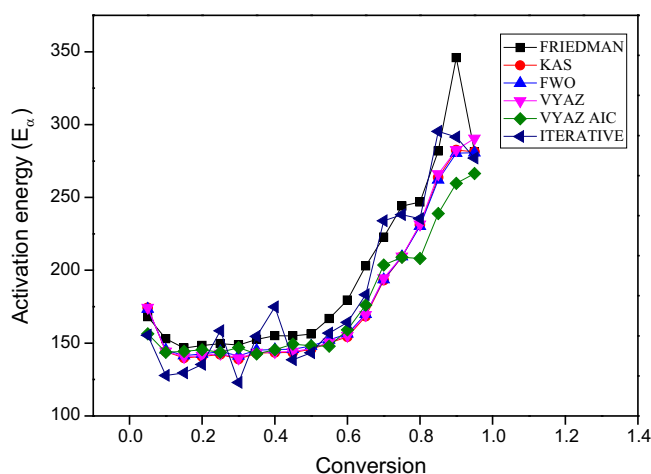


Fig. 2. Isoconversion plots for activation energy versus conversion.

The apparent activation energy values vary with conversion as the decomposition process proceeds indicating occurrence of a complex multistep mechanism. This variation helps in detecting the reaction model and pre exponential factor. Based on the trend of activation energy values the entire decomposition region can be divided into two stages. The apparent activation energies in the 5–60% conversion range have a value of 142–170 kJ/mol ($E_{avg} = 155.787$ kJ/mol) and 170–270 kJ/mol ($E_{avg} = 236.743$ kJ/mol) in the conversion range of 61–90% respectively.

3.3. Evaluation of pre-exponential factor and reaction mechanism

The E_a values obtained by Vyazovkin AIC method are used to predict the reaction mechanism and pre exponential factor for the process, since the method is found to be more efficient than the rest of isoconversional methods. Two methods are used for evaluation of reaction mechanism.

3.3.1. Using compensation parameters

E and A values are evaluated for all model functions from Table 1 for the six different heating rates using the Vyazovkin AIC equation. The reaction order models give a high regression coefficient ($R > 0.95$) and are selected for evaluation of compensation effect parameters using Eq. (15) for each heating rate. The compensation

parameters obtained are $\alpha^* = -5.3389$ and $\beta^* = 0.2045$ with $R = 0.9986$. These compensation parameters are used for evaluation of A_x at each conversion value using Eq. (16). The $\ln A_x$ values vary in the range of 25–50 s^{-1} with an average value of 32.53 s^{-1} . The $f(\alpha)$ is numerically evaluated using A_x and E_x values and is compared against the theoretical $f(\alpha)$ curves. The experimental and theoretical curves for $f(\alpha)$ are shown in Fig. 3a. Decomposition process for rice straw is a complex multi step reaction which is detected by the variation of activation energy with conversion. Therefore, the overall mechanism cannot be predicted by a single rate equation and different mechanisms are identified at different conversion ranges. When the conversion is less than 0.3 the experimental curve overlaps the D1, D2 curves. These decomposition mechanisms refer to diffusion in one and two dimensions, respectively. At conversion values greater than 0.3 the pyrolysis mechanism tends towards R3 curve which is a third order rate equation. The overall curve trend is similar to that for one and two dimension diffusion reactions D1 and D2, respectively (see Fig. 3b).

3.3.2. Using $z(\alpha)$ master plots

The experimental and theoretical $z(\alpha)$ curves are shown in 3b. The experimental curve is close to the $z(\alpha)$ curve for D2, D4 at conversion less than 0.3. These mechanisms refer to two dimensional diffusion and three dimensional diffusion–Ginstling Brounshtein equation respectively. The Ginstling Brounshtein equation refers to diffusion controlled reactions starting on the exterior of a spherical particle with radius r_0 . Khawam and Flanagan have explained the diffusion process of Ginstling Brounshtein equation in detail in their review article (Khawam and Flanagan, 2006). At higher conversions the curve is closest to R3 curve compared to any other model but is not superimposed on R3 i.e. third order rate equation.

The predictions from $z(\alpha)$ master plots are similar to those predicted by the use of compensation parameters. However, the predictions made by $z(\alpha)$ master plots are made in a model free way and hence the estimations from these plots are more crucial than those using compensation parameters. The experimental and theoretical $f(\alpha)$ curves for conversion greater than 0.3 are more close than those of $z(\alpha)$ master plots. This can be due to the effect of compensation parameters whose origin remains a subject of controversy. The non-Arrhenian character frequently observed for complex reactions and the use of an overall rate equation instead of the real complex rate equation, can lead to an apparent compensation effect between the preexponential factor and the activation energy if the overall rate is fitted into the Arrhenius equation (Budrugeac and Segal, 1998).

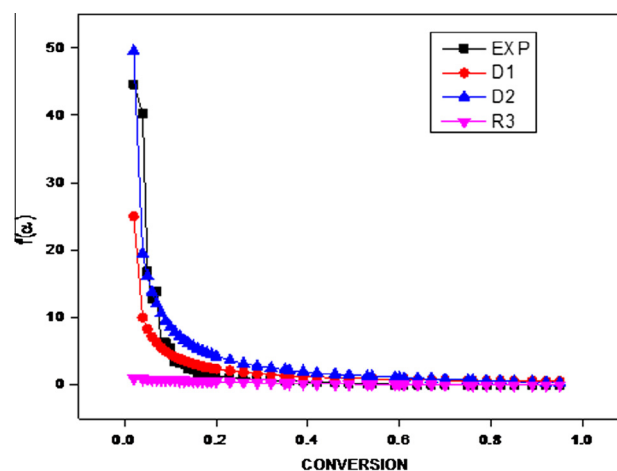


Fig. 3a. Experimental and theoretical $f(\alpha)$ curves.

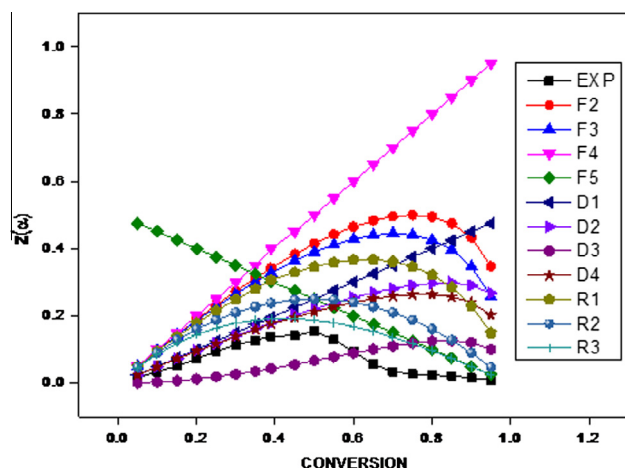


Fig. 3b. $z(\alpha)$ master plots for rice straw.

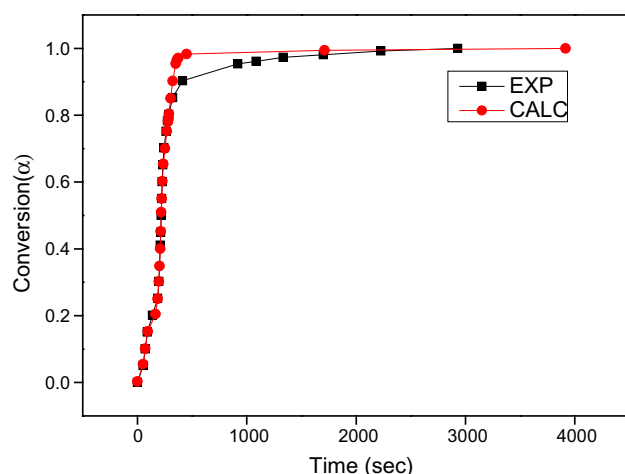


Fig. 4. Isothermal predictions at 400 °C.

Taro Sonobe et al. (2006) used rice straw samples from Thailand for studying the pyrolysis kinetics using a single stage distributed activation energy model and found the mean activation energy value to be 170 kJ/mol. This is in the range of the values reported in the present work but as he assumed a single Gaussian distribution the multi stage decomposition process could not be detected in the process which is shown in the present work. Ji et al. (2011) used the model fitting approach to study rice straw kinetics and found that the pyrolysis of rice straw can be represented best by a kinetic reaction model comprised of a two-step competitive reaction. The first step is three-dimensional nucleation/nucleus growth according to the Avrami/Erofeev reaction (A3), and the second is the third order reaction. The estimated activation energy was 131.9 and 138.85 kJ/mol. The use of model fitting methods leads to uncertain kinetic predictions where more than one model fits into the rate equation and lead to erratic results. The prediction of a third order rate equation at higher conversion values is also found in the present study using the method of compensation parameters. Hence the results are in good agreement with the reported data for rice straw kinetics and the discrepancies occur due to the difference in selection of kinetic evaluation methods. The model free kinetic methods are found to be superior in predicting the kinetic results as they include no early assumptions for the mechanism of the process.

3.4. Isothermal predictions from non-isothermal curves

The isoconversational analysis give a simple way to verify the validity of the kinetic predictions made using these models by predicting isothermal kinetics from the non-isothermal kinetic parameters. If a numerical method is trustworthy and applied with due care, it should fulfill the above expectations. Isothermal predictions can be made using the equation below,

$$t_{\alpha} = \frac{\int_0^T \exp\left(\frac{-E}{RT}\right) dT}{\beta \exp\left(\frac{-E}{RT_0}\right)} \quad (19)$$

where t_{α} is the time to reach the extent of conversion α at the temperature T_0 , (Burnham and Braun, 1999). For the case of isoconversational analysis, the sole evaluation of E_{α} dependence is sufficient to predict the isothermal kinetics from nonisothermal data. Vyazovkin and Lesnikovich in 1988 first derived the above equation. (Vyazovkin, 2001).

The E_{α} versus α values are used for isothermal predictions at 400 °C. The graph for isothermal prediction is shown in Fig. 4. The kinetic results made by isoconversational methods are validated since the above equation gives good predictions for isothermal run at 400 °C with less error.

4. Conclusion

Pyrolysis kinetics of rice straw was studied in TGA using model free methods. The Vyazovkin AIC method is found to be more suitable as it gives fewer errors and involves more accurate approximations. Multistep kinetics is detected from isoconversational plot indicating two zones with average activation energy of 155.787 and 236.743 kJ/mol. At conversion values less than 0.3 the decomposition of rice straw is governed by diffusion and it tends to third order rate equation at high conversion (predicted by compensation effect method). The isothermal predictions carried at 400 °C are in close agreement with the experimental curves and hence validate the kinetic analysis.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.biortech.2014.07.045>.

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